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Active control of oxygen in molten lead-bismuth eutectic systems to prevent steel corrosion and coolant contamination

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Abstract

The thermodynamic basis for controlling oxygen level in lead–bismuth to prevent steel corrosion and coolant contamination is examined. The operational conditions, including the thermodynamic activity of oxygen, cover gas oxygen partial pressure, mixtures of H_2 and H_2O (steam) to obtain such low oxygen partial pressure ($<10^{-24}$ atm or around 10^{-6} wt% in lead–bismuth), and the voltage signals of one type of oxygen sensors (with a solid electrolyte and molten bismuth reference electrode) are calculated. These results provide the guidance to implement the oxygen control technique. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

There are strong current interests worldwide in using lead and its alloys (particularly lead-bismuth eutectic, or LBE) for nuclear applications. The US DOE Advanced Accelerator Applications (AAA) Program, of which Accelerator-driven Transmutation of Waste (ATW) is a part, has been investigating LBE as a candidate for high power spallation neutron targets and coolant for the subcritical transmutation blanket with many other international programs [1]. The US DOE Generation IV Nuclear Energy Systems Initiative, and similar initiatives overseas, will examine lead and lead alloys based innovative reactor concepts.

Lead and LBE have exceptional chemical, thermal physical and nuclear properties for nuclear coolant applications. However, lead and LBE are also very corrosive to common steels used in nuclear installation. This has been widely recognized as one of the critical

*Tel.: +1-505 665 6677; fax: +1-505 665 6927. E-mail address: ningli@lanl.gov (N. Li). issues that need to be resolved before general use of lead and LBE coolants is accepted.

Due to the relatively high solubility of the major alloying components of steels, lead-bismuth can be severely corrosive to steels (via mass dissolution attack) if no protective means are applied. The solubility of Ni in LBE can reach a few weight percent at moderately high temperatures.

Early research on LBE nuclear coolant had made significant progress toward identifying the material compatibility issues, but the corrosion problems, esp., for steels, were not resolved. Some of the findings are briefly listed in the following [2–9].

- Carbon steels are the most corrosion resistant, low alloy steels (<2.25% Cr) are moderately corrosion resistant, and high Cr steels are subject to gross attack; refractory metals (Mo, W and Ta), graphite and some ceramics (alumina, silicon nitride, silica glass and alumina–silica glass) are impervious to LBE attack (but they are not very practical for large installations).
- Zr, Ti and Mg additives are variously used as inhibitors with limited but inconsistent success.

Coating the structural materials with nitride or oxide protective films beforehand failed to consistently prevent corrosion.

The second and third findings all point to the use of protective films for corrosion prevention. As is evidenced in the general industrial use of lead the presence of oxide films on common, inexpensive structural steels result in adequate performance. However, it was felt and found experimentally that in more advanced uses of lead or LBE, where long service life and minimum contamination were required, the chemical conditions made it difficult to maintain and repair a protective oxide film.

Coating the structural materials with nitride or alumina films were tested. However, it is difficult to maintain the integrity of the films since abrasion and cuts take place during handling and installation. The films can further lift, spall, and flake during operation due to differential thermal expansion and other factors. Experiments found severe corrosion when the films failed and no repair mechanism was readily available during testing.

Adding inhibitors such as titanium or zirconium to form protective layers of carbide or nitride requires that the correct concentration of inhibitors is maintained in the liquid metal and there is an adequate reserve of carbon or nitrogen in the steel. For long service life materials, there is limited carbon and nitrogen in steels for continued addition of inhibitors to heal any damaged protective films. The depletion of these minor elements could adversely affect the properties of the steels. The contamination of the liquid metal by inhibitors is not desirable in the long run as well.

Most damagingly, it was found that pre-oxidation of steels would not prevent mass transfer corrosion through oxygen exchange in non-isothermal lead and bismuth systems based on thermodynamic consideration [9]. Fe₃O₄ based oxide protective film can be reduced by lead and bismuth if little or no iron exists in the melt, as would be the case when the film shields rather pure lead and bismuth from the substrate Fe. Due to the temperature dependence of this reaction, Fe in lead and bismuth will remain below the equilibrium value in the hottest areas, and gradual removal of oxide layer will ensue. Since this has been observed experimentally, it would appear that using oxide film for protection is not a practical means for preventing corrosion of steels.

However, the kinetics of the above reduction reaction could drastically reduce the Fe transfer rate if the oxygen level is actively maintained at proper levels. We will systematically examine the thermodynamic data for the various reactions and find the allowable operating conditions, and establish the basis for the oxygen control technique.

Since this paper was first written, there has been significant progress in the study of LBE corrosion.

Many of the experimental results support, sometimes only qualitatively at this stage, the theory and calculation outlined here. For instance, the release of corrosion study data from Russian [10], and the LBE corrosion tests of European, Japanese and US steels [11,12] all confirmed the basic validity of oxygen control for corrosion prevention. A more systematic kinetic modeling of corrosion in LBE with oxygen control confirmed the potential for significant reduction of corrosion [13]. Oxygen sensors are being developed and tested [14–16]. Many ongoing experiments around world are aiming to map the corrosion rates, improve oxygen sensors and control systems. In particular, our project has designed and constructed a medium-scale forced circulation LBE materials test loop to further develop this technology and test materials [17].

2. Thermodynamic basis for oxygen control

Unlike many other liquid metal coolants (Na, Li, NaK, and Pb–17Li), lead and bismuth are chemically more inert than the major alloying elements in steels (Fe, Ni, and Cr). This is demonstrated in the molar free energy of formation of the oxides (Fig. 1): the lower the free energy, the easier it is to form the corresponding oxide. It is thus possible to 'passivate' the surface of the structural steels in contact with lead and bismuth by proper oxygen level control, such that a 'self-healing' protective oxide film forms to prevent steel corrosion, while no excess oxygen is present to form lead and/or bismuth oxide precipitants to contaminate the coolant.

For the following thermodynamic calculations, we used the free energy of formation data from 'The Oxide Handbook' [18] and the solubility data from the presentations by specialists from the Institute of Physics and Power Engineering (IPPE) [19] (Fig. 2).

The temperature dependence of the free energy formation can be generally expressed as

$$\Delta F^0 = A_1 + B_1 T,\tag{1}$$

and the solubility in LBE can be expressed as

$$\log c_{\rm s} = A_2 + B_2/T. \tag{2}$$

The values of A_i and B_i for the relevant species are tabulated in Tables 1 and 2 (Na data is included to provide comparison).

For a system of metal M, its oxide M_xO_y and oxygen, the reaction is

$$\frac{x}{y}\mathbf{M}_{(s)} + \frac{1}{2}\mathbf{O}_{2(g)} = \frac{1}{y}\mathbf{M}_{x}\mathbf{O}_{y(s)}$$
 (3)

and the equilibrium constant is

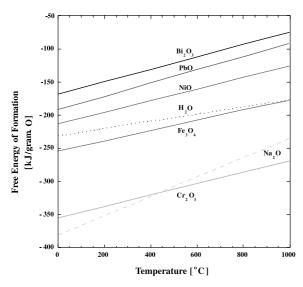


Fig. 1. Free energy of formation for the various species in steels and lead-bismuth. Sodium data is provided for comparison.

$$K = \frac{a_{M_{x}O_{y(s)}}^{1/y}}{a_{M(s)}^{x/y}a_{O_{2(u)}}^{1/2}} = \exp\left(-\frac{1/y\Delta F_{M_{x}O_{y}}^{0}}{RT}\right). \tag{4}$$

If the condition exists for the formation of the standard state of M_xO_y , then $a_{M_xO_y} = 1$, and

$$K = \frac{1}{P_{O_2}^{1/2}} = \exp\left(-\frac{1/y\Delta F_{M_xO_y}^0}{RT}\right),\tag{5}$$

or

$$\log P_{\rm O_2} = \frac{2/y \Delta F_{\rm M_x O_y}^0}{2.303RT} = \frac{2/y (A_1 + B_1 T)}{2.303RT} = A_3 + \frac{B_3}{T}.$$
 (6)

The constants $A_3 = 0.1045B_1/y$, $B_3 = 0.1045A_1/y$ are tabulated in Table 3.

In particular, if Fe is exposed to oxygen (O_2) , e.g. in the cover gas space, the reaction is

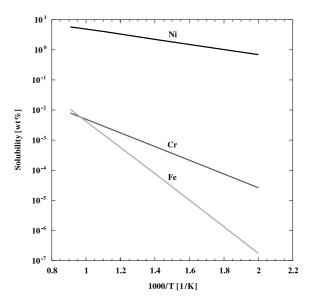


Fig. 2. The solubility of several major alloying components of steels in LBE (data according to IPPE [19]).

$$\frac{3}{4}Fe_{(s)} + \frac{1}{2}O_{2(g)} = \frac{1}{4}Fe_3O_{4(s)}$$
 (7)

and the equilibrium constant is

$$K_{1} = \frac{a_{\text{Fe}_{3}\text{O}_{4(s)}}^{1/4}}{a_{\text{Fe}_{3}\text{O}_{4}}^{3/4}a_{\text{O}_{2(g)}}^{1/2}} = \frac{1}{P_{\text{O}_{2}}^{1/2}} = \exp\left(-\frac{1/4\Delta F_{\text{Fe}_{3}\text{O}_{4}}^{0}}{RT}\right), \tag{8}$$

where $a_{\text{Fe}_3\text{O}_4}$ and a_{Fe} are unity (Fe₃O₄ is assumed to be non-soluble in lead and bismuth). We can similarly write down the reactions and equilibrium conditions for Ni and Cr. Since Cr has a larger free energy of formation than Fe, Cr₂O₃ is formed before Fe₃O₄ formation. However, Russian experience suggests that Fe₃O₄ is the base of the protective film [19,20].

For lead oxide to precipitate from lead exposed to oxygen,

$$Pb + \frac{1}{2}O_{2(g)} = PbO_{(s)}$$
 (9)

Table 1
The free energy of formation data (according to Oxide Handbook)

ΔF^0 (J/mol)	Bi ₂ O ₃	PbO	NiO	Fe ₃ O ₄	Cr ₂ O ₃	H ₂ O	Na ₂ O
A_1	-582070	-220670	-237520	-1108300	-1137700	-245570	-420370
B_1	282.0	101.0	88.04	313.3	260.5	54.45	145.6

Table 2 Solubility data (according to IPPE)

$C_{\rm s}$ (wt%)	Ni	Fe	Cr	0
A_2	1.53	2.01	-0.02	1.2
B_2	-843	-4380	-2280	-3400

Table 3
Partial pressure of oxygen for oxide formation

$\log P_{\mathrm{O}_2}$ (atm)	Bi_2O_3	PbO	NiO	Fe ₃ O ₄	Cr ₂ O ₃	Na ₂ O
A_3 B_3	$9.82 \\ -20275$	10.55 -23060	9.20 -24821	8.19 -28 954	9.07 -39 630	15.22 -43 929

$$K_2 = \frac{a_{\text{PbO}_{(s)}}}{a_{\text{Pb}} a_{\text{O}_{2(e)}}^{1/2}} = \frac{1}{P_{\text{O}_2}^{1/2}} = \exp\left(-\frac{\Delta F_{\text{PbO}}^0}{RT}\right),\tag{10}$$

where $a_{PbO} = 1$. Since bismuth has a smaller free energy of formation than lead, bismuth oxide will not form until significant amount of lead oxide is already formed.

Clearly, the above two partial pressures of oxygen in the cover gas of a lead and bismuth system define the extremes of the oxygen conditions allowed. If the oxygen partial pressure is too low, then the steels cannot form a protective oxide film and will be exposed to lead and bismuth and subject to dissolution and mass transfer corrosion. If the oxygen level is too high, lead oxide will precipitate to contaminate the coolant and degrade the thermal hydraulic performance.

The situation is more complex at the surfaces of the structural steels submersed in lead and bismuth. The key insight is the inhomogeneous and non-localized nature of reactions involving Fe (Ni, Cr), Pb (Bi), O and the corresponding oxides. The kinetics of the reaction and reactants distribution become very important.

3. Operating conditions for oxygen control

It is illustrative to find out the oxygen concentration in lead and bismuth within the range of partial pressures determined above. Due to the mixing turbulent flows, it can be reasonably expected that the oxygen concentration is uniform in the bulk of lead and bismuth, and it should be in equilibrium with the oxygen in the cover gas. Since it is generally easier to control the oxygen partial pressure in the cover gas with some chemical reactions, this relation between oxygen concentration and partial pressure should be useful. However, as it has been shown, measuring oxygen concentration or its thermodynamic activity in lead and bismuth can be achieved reliably with solid electrolyte sensors.

The above assumption should be carefully examined if pool-type system is considered: the lack of a strong and all-reaching mixing flow in this type of system may render the current analysis inapplicable. Also, if there is excess oxygen in the cover gas and lead oxide precipitates at the interfacial surface, the oxygen in lead and bismuth is at the solubility limit and not in equilibrium with the oxygen in the cover gas. This condition should only be allowed to occur when the cover gas is at the coldest part of the system, because otherwise lead oxide

will precipitate onto parts of structural surfaces with temperatures lower than the cover gas. In effect, this is the condition for the cold-trap operation.

In a system of oxygen in the cover gas, oxygen in lead and bismuth, lead and lead oxide,

$$Pb + \frac{1}{2}O_{2(g)} = PbO_{(Pb)} \tag{11}$$

$$K_{2} = \frac{a_{\text{PbO}_{(\text{Pb})}}}{a_{\text{Pb}} a_{O_{2(s)}}^{1/2}} = \frac{c_{\text{O}}/c_{\text{s,O}}}{P_{\text{O}_{2}}^{1/2}} = \exp\left(-\frac{\Delta F_{\text{PbO}}^{0}}{RT}\right), \tag{12}$$

where $a_{\rm PbO_{(Pb)}} = c_{\rm O}/c_{\rm s,O}$ according to Henry's law, $c_{\rm O}$ is the oxygen concentration, and $c_{\rm s,O}$ is the oxygen solubility in lead and bismuth. So the relationship between oxygen partial pressure and concentration can be derived as

$$\log P_{\rm O_2} = 2 \left(\log c_{\rm O} - \log c_{\rm s,O} + \frac{\Delta F_{\rm PbO}^0}{2.303RT} \right)$$

$$= 2 \log c_{\rm O} + 8.16 - \frac{16261}{T}. \tag{13}$$

The relations among oxygen partial pressure for various metal oxides formation and the corresponding oxygen concentration in lead and bismuth are shown in Fig. 3.

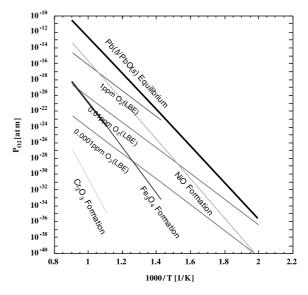


Fig. 3. The oxygen partial pressures for various oxides formation and oxygen concentrations in LBE.

Obviously, if the oxygen concentration is low enough so that no lead oxide precipitation occurs at the coldest part of the system, then there should be no lead oxide precipitation anywhere. Conversely, if the oxygen concentration is sufficiently high for forming Fe_3O_4 protective film at the hottest part, there the favorable condition exists everywhere in the system.

4. Self-healing film

However, the film formation on structural surfaces submersed in lead and bismuth warrants a closer look since a continuous film separates the substrate metal completely from the lead and bismuth.

The reaction on the protective Fe₃O₄ film on structural surfaces submersed in lead and bismuth is (assuming Fe₃O₄ is insoluble)

$$\frac{1}{4}Fe_3O_{4(s)} + Pb = \frac{3}{4}Fe_{(Pb)} + PbO_{(Pb)}$$
 (14)

$$K_{3} = \frac{a_{\text{PbO}_{(\text{Pb})}} a_{\text{Fe}_{(\text{Pb})}}^{3/4}}{a_{\text{Pb}} a_{\text{Fe}_{3}\text{O}_{4(s)}}^{1/4}} = \left(\frac{c_{\text{O}}}{c_{\text{s,O}}}\right) \left(\frac{c_{\text{Fe}}}{c_{\text{s,Fe}}}\right)^{3/4}$$
$$= \exp\left(-\frac{\Delta F_{\text{PbO}}^{0} - 1/4 \Delta F_{\text{Fe}_{3}\text{O}_{4}}^{0}}{RT}\right). \tag{15}$$

If there is none or little Fe in lead and bismuth (as it should be for clean lead and bismuth coolant), then the above reaction proceeds to the right and Pb begins to destroy the Fe₃O₄ film (Fig. 4). Assuming that the oxygen concentration is held constant through oxygen control and turbulent mixing flow, then the reaction stops when the Fe concentration near the interface reaches equilibrium. This concentration of Fe is orders of magnitude lower than the Fe solubility in lead and bismuth, and the rate of corrosion via dissolution is significantly reduced [13]. At this slow rate, oxygen diffusion through the film may be fast enough to regenerate the film on the substrate metals. Thus the protective film is self-healing.

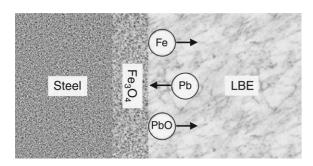


Fig. 4. The dynamic process of lead reducing iron oxide film and iron reforming oxide constitutes the self-healing protective oxide film formation.

The above process would not work if the oxygen concentration is left to its own device: if the oxygen concentration is allowed to decrease while the protective film is being destroyed, the Fe concentration will keep increasing until it reaches solubility near the interface. The resulting dissolution corrosion would be too severe for safe long-term operation.

This self-healing process in the protective film also points to the need for a complete preconditioning for parts used at relatively high temperatures since the unprotected steels may be corroded via dissolution too quickly to establish the protective film.

5. Oxygen thermodynamic activity in lead-bismuth

It would become evident that the oxygen thermodynamic activity (OTA) in lead and bismuth is a convenient and measurable parameter to work with.

From Eqs. (8) and (12), we find that the minimum OTA for Fe_3O_4 formation is

$$\log a_{\min}^{(\text{Fe}_{3}\text{O}_{4})} = \log \left\{ P_{\text{O}_{2},\text{Fe}_{3}\text{O}_{4}}^{1/2} \exp \left(-\frac{\Delta F_{\text{PbO}}^{0}}{RT} \right) \right\}$$

$$= \frac{1/4 \Delta F_{\text{Fe}_{3}\text{O}_{4}}^{0} - \Delta F_{\text{PbO}}^{0}}{2.303RT}$$

$$= -1.19 - \frac{2948}{T}, \tag{16}$$

below which the steels are subject to rather severe dissolution corrosion. The maximum OTA for the lead—bismuth system is 1, beyond which lead oxide will precipitate.

The oxygen concentration in lead and bismuth is simply related to OTA via

$$\log a_{\rm O} = \log c_{\rm O} - \log c_{\rm s,O} = \log c_{\rm O} - 1.2 + \frac{3400}{T}.$$
 (17)

We can express the relation of Fe concentrations to OTA similarly: from Eq. (15), we obtain

$$\log a_{\rm O} = -\frac{3}{4} (\log c_{\rm Fe} - \log c_{\rm Fe,0}) + \frac{1/4 \Delta F_{\rm Fe,O_4}^0 - \Delta F_{\rm PbO}^0}{2.303 RT} = -\frac{3}{4} \log c_{\rm Fe} + 0.318 - \frac{6233}{T}.$$
 (18)

Plotting $\log a_{\min}$, $c_{\text{Fe}} = \text{const}$ and $c_{\text{O}_2} = \text{const}$ together is a very useful illustration of the oxygen control process (Fig. 5) [19]. Coolant contamination via oxidation of Pb takes place in the region above $a_{\text{O}} = 1$, and steel corrosion via dissolution occurs below a_{\min} since Fe₃O₄ film is unstable. Between these two extremes, a Fe₃O₄-based film can form on the surfaces of steels to protect them from LBE corrosion, but the film is subject to LBE reduction if the concentration of Fe is too low in the LBE

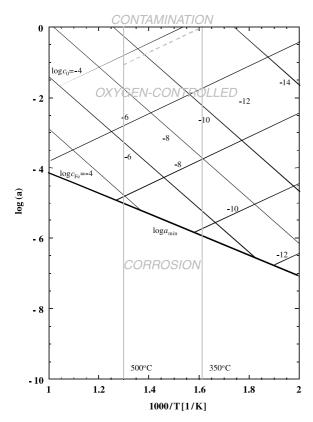


Fig. 5. The regime of thermodynamic activity of oxygen in LBE for proper oxygen control to prevent corrosion and contamination.

next to the film. One cannot find a static equilibrium because the temperature dependence of constant oxygen concentration do not coincide that for the constant Fe concentration, while in a turbulent mixing LBE flow systems both are roughly constant in the bulk of LBE. However, if the oxygen concentration is maintained such that lead oxide can almost precipitate in the coldest region (cold-trap condition), then the Fe concentration near the steel surfaces can be orders of magnitude lower than the Fe solubility in LBE. This in turn reduces the corrosion rate by orders of magnitude.

6. Oxygen sensor signals

The oxygen sensors used for applications of liquid metals are usually of solid electrolyte types. The oxygen concentration difference across the solid electrolyte and the resultant oxygen ion conduction inside the electrolyte establishes an EMF that can be measured to indicate the oxygen concentrations.

Sensors with solid electrolyte and molten bismuth saturated with oxygen have been used successfully in the Russian nuclear coolant applications (Fig. 6) [14,19],

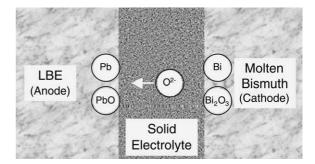


Fig. 6. Schematic of the electrochemical cell in one type of solid electrolyte oxygen sensor.

and are being developed and tested elsewhere [15,16]. We will determine the expected signal output at the oxygen control operation conditions.

For the system of Pb, PbO, oxygen permeable solid electrolyte, Bi and Bi₂O₃ (saturated—exposed to the air), the reaction is

$$Pb + \frac{1}{3}Bi_2O_{3(Bi)} = PbO_{(Pb)} + \frac{2}{3}Bi.$$
 (19)

According to the Nernst equation, the potential difference across the electrolyte is

$$E = E_{\text{PbO}}^{0} - E_{\text{Bi}_2\text{O}_3}^{0} - \frac{RT}{2F} \ln \frac{a_{\text{Bi}}^{2/3} a_{\text{PbO}}}{a_{\text{Pb}} a_{\text{Bi}_2\text{O}_3}^{1/3}}$$

$$= \frac{1/3 \Delta F_{\text{Bi}_2\text{O}_3}^{0} - \Delta F_{\text{PbO}}^{0}}{2F} - \frac{RT}{2F} \ln a_{\text{PbO}}.$$
(20)

Using the Oxide Handbook data

$$\log a_{\text{PbO}} = -\frac{10083}{T}(E - 0.1381) - 0.366. \tag{21}$$

The available IPPE result is

$$\log a_{\text{PbO}} = -\frac{10094}{T}(E - 0.088) - 0.18. \tag{22}$$

According to the IPPE specialists, their result is more accurate because all the relevant parameters were measured under the same conditions.

Since we are interested in the signal output, we can convert the previously obtained ranges of OTA to E. The maximum E corresponds to the minimum a, above which steel corrosion takes place. From the Oxide Handbook data,

$$E_{\text{max}}^{(\text{Fe}_3\text{O}_4)} = 8.17 \times 10^{-5} T + 0.431 \text{ [V]}.$$
 (23)

According to the IPPE data,

$$E_{\text{max}}^{(\text{Fe}_3\text{O}_4)} = 7.42 \times 10^{-5} T + 0.442 \text{ [V]}. \tag{24}$$

The minimum E corresponds to a=1, below which lead oxide precipitation takes place. From the Oxide Handbook data,

$$E_{\min} = -3.63 \times 10^{-5} T + 0.1381 \text{ [V]}.$$
 (25)

According to the IPPE data,

$$E_{\min} = -1.78 \times 10^{-5} T + 0.088 \text{ [V]}.$$
 (26)

The difference between results from two data sources is appreciable at E_{\min} but remains small throughout the relevant temperature range for E_{\max} (Fig. 7).

Because of the turbulent mixing flow in the typical lead and bismuth coolant systems, it is the oxygen concentration rather than OTA that is constant throughout. More likely than not, the oxygen in the melt is in equilibrium with the oxygen in the cover gas at the coldest part of the system. Since the oxygen sensors usually do not work reliably till well above 300 °C for the lack of sufficient oxygen diffusion in the solid electrolyte at low temperatures, it would be useful to map out E vs. T regions for the existence of proper conditions throughout the systems. This would ensure that through measuring OTA at a workable temperature and location we can detect possible coolant contamination conditions at the coldest part where oxygen sensors may not work properly. Conversely, we can also detect possible corrosion conditions at the hottest part where it is difficult to insert oxygen sensors, such as in a spallation target, or in reactor cores.

According to the previous discussion on the magnitude of reduction in corrosion, it appears optimal to run the system near the cold-trap condition. This implies that we should operate with E_{\min} at the coldest part of the system, where $T = T_{\rm c}$. According to Eq. (21),

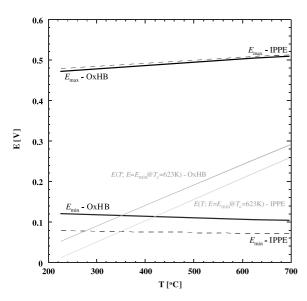


Fig. 7. Solid electrolyte oxygen sensor signal output for various oxygen control regimes.

$$E(T) = -9.92 \times 10^{-5} T (\log c_{s,O}(T_c) - \log c_{s,O}(T) + 0.366) + 0.1381$$

= -3.63 \times 10^{-5} T - 0.199 + \frac{0.337T}{T_c}. (27)

According to Eq. (22),

$$E(T) = -1.78 \times 10^{-5} T - 0.249 + \frac{0.337T}{T_c}.$$
 (28)

The results are shown in Fig. 7 for $T_c = 350$ °C (623 K).

7. Cover gas oxygen partial pressure and mixture of H_2/H_2O

There are several ways to control the oxygen level. One of them is to control the oxygen partial pressure in the cover gas system. Since the required oxygen level is very low, direct control is difficult. However, there are several chemical reaction systems where the partial pressure of oxygen is controlled by the ratio of other gases involved, e.g. the O₂/H₂/H₂O and O₂/CO/CO₂ systems. The former is particularly attractive since H₂ can be used to reduce PbO contaminant as well.

In the reaction of

$$H_2 + \frac{1}{2}O_2 = H_2O \tag{29}$$

the reaction equilibrium constant is

$$K = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}P_{\text{O}_2}^{1/2}} = \exp\left(-\frac{\Delta F_{\text{H}_2\text{O}}^0}{RT}\right). \tag{30}$$

It is evident then that the ratio of H_2 and H_2O determines the partial pressure of oxygen. Following Eq. (8), the required mixture of H_2 and H_2O for the formation of Fe_3O_4 is

$$\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} = P_{\text{O}_2}^{1/2} \exp\left(-\frac{\Delta F_{\text{H}_2\text{O}}^0}{RT}\right) \\
= \exp\left(-\frac{\Delta F_{\text{H}_2\text{O}}^0 - 1/4\Delta F_{\text{Fe}_3\text{O}_4}^0}{RT}\right) \\
= 10^{1.25 - 1646/T} \tag{31}$$

Following Eq. (9), the required mixture for the formation of PbO is

$$\frac{P_{\rm H_2O}}{P_{\rm H_2}} = \exp\left(-\frac{\Delta F_{\rm H_2O}^0 - \Delta F_{\rm PbO}^0}{RT}\right) = 10^{2.43 + 1301/T}$$
 (32)

These two equations determine the range out of which either corrosion or contamination occurs (Fig. 8). From the previous discussion, the mixture in the cover gas

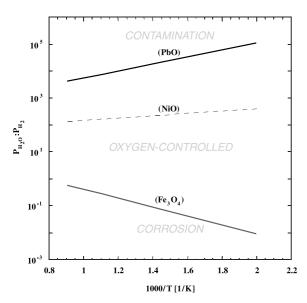


Fig. 8. H₂ and H₂O mixture in the cover gas for controlling oxygen levels.

should be near the boundary determined by PbO formation.

8. Conclusion

Using the available thermodynamic and solubility data from several different sources, we have established the feasibility of using active oxygen control in lead and bismuth systems to prevent corrosion and contamination. We have also constructed the plausible operating conditions, the oxygen sensor signals, and the means to achieve the desired oxygen level.

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